

NRC INSPECTION MANUAL

ECEB

INSPECTION PROCEDURE 79501

LWR WATER CHEMISTRY CONTROL AND CHEMICAL ANALYSIS - AUDITS

PROGRAM APPLICABILITY: 2513, 2515

79501-01 INSPECTION OBJECTIVES

01.01 To determine the licensee's capability to control the chemical quality of plant process water in order to minimize corrosion and out-of-core radiation field buildup, thereby reducing occupational radiation exposures.

01.02 To determine the licensee's capability for making the chemical measurements necessary for control of the chemical quality of plant process water.

79501-02 INSPECTION REQUIREMENTS

02.01 Establishment of a Water Chemistry Control Program. Determine whether the licensee has established an effective, documented program for controlling the quality of primary coolant water and PWR secondary water including:

- a. management policies including management commitment to, and support for, an effective program
- b. procedures to implement policies
- c. assignment of authority and responsibilities to carry out the program
- d. adequate resources of staffing, equipment, funds and organization to implement an effective program

02.02 Implementation of the Water Chemistry Control Program. Determine whether the water chemistry control program is being implemented in accordance with existing policies and procedures.

02.03 Water Sampling. Determine the adequacy of provisions for obtaining samples of water for chemical analyses that are used for water chemistry controls.

02.04 Chemistry Measurements: Facilities and Equipment. Determine whether the following meet licensee commitments and are adequate to provide quality measurements of chemical variables:

- a. chemistry laboratory and laboratory equipment

- b. on-line monitors for measurements of chemical variables

02.05 Establishment of a Quality Assurance Program for Chemical Measurements. Determine whether a quality assurance program has been established for chemical measurements that meets licensee commitments and is adequate for use in controlling chemical variables.

02.06 Implementation of a Quality Assurance Program for Chemical Measurements. Determine whether the water chemistry control program is being implemented in accordance with existing policies and procedures.

02.07 Laboratory Safety. Note departures from prudent practices for ensuring the non-radiological health and safety of laboratory workers.

79501-03 INSPECTION GUIDANCE

03.01 Water Chemistry Control Program

- a. This inspection procedure complements IE Inspection Procedure 79502, "Plant Systems Affecting Plant Water Chemistry".
- b. The Electric Power Research Institute (EPRI) sponsors numerous research and development projects on minimizing corrosion and on radiation buildup by use of water chemistry controls. These projects are described in EPRI reports and the results are summarized in articles in the EPRI Journal and other technical periodicals. Many of these publications are included in the Bibliography (Section 4). The industry-sponsored research and development has made it clear that maintenance of good water chemistry will cost less than the repair and replacement of reactor coolant system components, steam generators, or nuclear fuel and the outages associated with these efforts. Thus, there are strong economic incentives for good water chemistry in addition to the occupational dose savings that will result from avoidance of the need for these repair and replacement activities.
- c. For PWRs, Technical Specifications usually include limits and associated surveillance requirements for boron, dissolved oxygen, chloride, fluoride, and radioactivity concentrations in reactor coolant water. PWR Technical Specifications (under "Administrative Controls") also usually require a program for monitoring the secondary water chemistry to inhibit steam generator tube degradation. Branch Technical Position MTEB 5-3, which is appended to Standard Review Plan Section 5.4.2.1, provides guidance on this topic as does the industry report, EPRI NP-2704-SR, "PWR Secondary Water Chemistry Guidelines". These guidelines were prepared by a committee of experienced utility industry personnel to aid in the use of PWR secondary water chemistry to minimize localized corrosion in steam generators and turbines. In the report, water chemistry control parameters are justified, and the available analytic methods, the data management and surveillance, and the management philosophy required to successfully implement the guidelines are summarized. These guidelines apply to cold shutdown (when layup is needed), as well as to the hot standby, startup and power status modes. Guideline parameters are provided for samples of feedwater, blowdown, and condensate. The guidelines include the following chemical determinations for water chemistry control: specific conductivity, cation conductivity, suspended solids, pH, ammonia, chloride, dissolved oxygen, hydrazine, silica, copper, iron, sulfate and sodium.

- c. For BWRs, Technical Specifications usually include limits and associated surveillance requirements for pH, conductivity, chloride, and radio-activity concentrations in reactor coolant water. Regulatory Guide 1.56 provides guidance on "Maintenance of Water Purity in Boiling Water Reactors."
- d. BWR Water Chemistry Guidelines, similar to the PWR Secondary Water Chemistry Guidelines, have been prepared by a committee of experienced utility industry personnel. These guidelines include suggested generic water chemistry specifications for reactor water, feedwater, condensate and control rod drive cooling water; justifications for the proposed water chemistry limits; suggested response to out-of-specification water chemistry; discussions of available chemical analysis methods and data management and surveillance schemes; and the management philosophy required to successfully implement water chemistry control guidelines. An appendix presents information on hydrogen water chemistry which provides an improved means of controlling corrosion problems in BWRs; NRC encourages the use of hydrogen water chemistry. The BWR Water Chemistry Guidelines apply to the operational status modes of cold shutdown, startup/hot standby, and power operation. The guidelines include the following chemical determinations for water chemistry control: conductivity (specific conductance), chloride, dissolved oxygen, iron, copper, and silica. In addition, the guidelines include the following chemical determinations for diagnostic use: sulfate, fluoride, purgable organics, total organic carbon, sodium, electrochemical potential, carbonate, pH, and nitrate. Use of radionuclide determinations and cation conductivity are also suggested for diagnostic use.
- e. Documentation of the water chemistry control program policies and procedures may include:
 - 1. statement of the need for a policy on, and goals/objectives of a chemistry control program
 - 2. management commitment to, support for, and control of the program
 - 3. assignment of responsibilities for preparation and approval of procedures to implement the policy and periodic review, evaluation, and updating of the program
 - 4. quality assurance for the water chemistry control program
 - 5. identification of the critical chemical variables and limit/action levels for control of these variables during all phase of plant operation
 - 6. identification of variables to be monitored continuously (online) and locations of continuous monitors
 - 7. identification of locations for taking grab samples, sampling schedules, and provisions for obtaining representative samples
 - 8. identification of procedures used for analysis of samples and the basis for the procedure (e.g., ASTM number)
 - 9. procedures for recording and management of water quality data, including trending of chemical and radio-chemical data
 - 10. provisions for preventing the introduction of chemical contaminants, including organic chemicals, into primary and secondary coolant water, and detecting the presence of these contaminants; e.g., detecting organic chemicals by total organic carbon (TOC) analysis

11. procedures for control of chemicals and reagents used in primary and secondary water chemistry control and analysis (IE Manual Chapter 9900, "Applicability of Appendix B to Chemicals and Reagents")
 12. procedures defining investigative (diagnostic) or corrective actions to be taken when critical chemical variables exceed action levels or limits, and allowable times for taking these actions
 13. identification of individual responsibilities for reviewing and interpreting in-plant water quality data for acting on the result of these reviews and interpretations, and for resolving disagreements
- f. Regulatory Guide 1.33 includes Chemical and Radiochemical Control Procedures among safety-related activities that should be covered by procedures.
 - g. Adequacy of the chemistry staff is covered under IE Inspection Procedures 83522 and 83523. INPO guidance on "Chemistry Technician Qualification" is given in INPO 82-007. (INPO defines chemistry technicians as persons who perform qualitative and quantitative chemical analyses, prescribe chemistry control measures based on such analyses, and operate chemistry-related equipment.) A training (including retraining) program for everyone involved with water chemistry control should include the latest technical information, consequences of poor chemistry control, means for recognizing adverse conditions and trends, and corrective actions.

03.02 Implementation of the Water Chemistry Control Program. Examination of the implementation of the water chemistry control program may include:

- a. reviews of the results of audits and appraisals performed by or for the licensee and the licensee's responses to any identified needs for corrective actions
- b. reviews of records of completed chemical analyses to determine whether the analyses have been completed on schedule
- c. reviews and discussions of the recorded trends of water quality data
- d. reviews of investigative (diagnostic) and corrective actions taken when chemical variables have exceeded the established levels or limits, including consideration of the timeliness of these actions
- e. discussions with individuals at all levels who are involved with water chemistry controls to determine whether they understand the need for, and importance of, these controls and whether the individuals understand their roles in maintaining water quality

03.03 Water Sampling

- a. Sampling of liquid wastes, liquid effluents, and postaccident primary coolant sampling are covered by Inspection Procedure 84523.
- b. Guidance on good design practice is included in Standard Review Plan Section 9.3.2, "Process and Post-Accident Sampling Systems," and Section 11.5, "Process and Effluent Radiological Monitoring Instrumentation and Sampling Systems." Additional guidance on sampling is given in ASTM Standards D 1066, "Practice for Sampling Steam" D 1192, "Specification for Equipment for Handling Water and Steam," and D 3370, "Practices for Sampling Water."

- c. Sample collection points should be easily accessible, properly shielded, and properly ventilated.
- d. Representativeness of sampling may be determined by:
 - 1. verification of sample line input and source
 - 2. operability of purge and recycle of sample lines
 - 3. verification of tank volumes and recirculation times (where applicable)
 - 4. verification of sample line flush times
 - 5. verification of the use of approved sampling procedures and valve lineups

03.04 Chemistry Measurements: Facilities, and Equipment

- a. The PWR Secondary Water Chemistry Guidelines and BWR Water Chemistry Guidelines both contain specific recommendations on continuous monitoring of particular chemical parameters. ASTM STP 742 includes information on instrumentation for continuously measuring high-purity water quality. In considering continuous on-line monitors, include, as a minimum:
 - 1. For BWRs, the instruments, procedures, and calibration for measuring conductivity as discussed in Regulatory Guide 1.56, and the calibrations of these instruments, as discussed in ASTM D 1125.
 - 2. For PWRs, the instruments, procedures, and calibration for measuring pH and conductivity in secondary coolant water as discussed in Branch Technical Position MTEB 5-3 and ASTM D 1125.
- b. Guidance on laboratory facilities and equipment is available in the following documents:
 - 1. Subsection 7.3, "Physical Resources," in ASTM D 3856-80, "Evaluating Laboratories Engaged in Sampling and Analysis of Water and Waste Water."
 - 2. Chapter 2, "Laboratory Services," and Chapter 3, "Instrument Selection," in EPA-600/4-79-019.
 - 3. Chapter 3, "Laboratory Facilities and Services," in Quality Assurance Practices for Health Laboratories.
- c. The industry water chemistry guidelines (PWR secondary, and BWR), ASTM STP 742, and the paper by Siegwarth provide information on laboratory instrumentation for measurement of high-purity water quality.
- d. For chemistry laboratories, by review of plans and blueprints, by direct observations, and discussions with staff, determine the adequacy of the following:
 - 1. laboratory size and layout
 - 2. laboratory bench space, hood space, and storage space
 - 3. laboratory lighting, heating, ventilating, and air conditioning

4. laboratory services (distilled/demineralized water, compressed air, vacuum, electrical services)
5. instrumentation for analytical chemistry; e.g., analytical balance, atomic absorption spectrophotometer, conductivity bridge, gas chromatograph, pH meter, selective ion electrodes, turbidimeter, ultravioletvisible spectrophotometer, total organic carbon (TOC) analyzer, and ion chromatograph

03.05 Establishment of a Quality Assurance Program for Chemical Measurements

- a. Use of "confirmatory measurements" by NRC inspectors for checking in-plant radiochemical analyses is covered by Inspection Procedure 84525. Inspection Procedure 84525 also covers quality assurance for radiochemical analysis and postaccident chemical and radiochemical measurements; however, when "postaccident" instrumentation for chemical analysis is also used for routine analysis, the routine use should be covered by this procedure.
- b. Guidance on quality assurance for radiochemical analysis is given in Regulatory Guide 4.15. The basic quality assurance program elements given in that guide that also apply to chemical analysis follow:
 1. Organizational Structure and Responsibilities of Managerial and Operational Personnel (Inspection Procedure 83522)
 2. Specification of Qualifications of Personnel (Inspection Procedure 83523)
 3. Operating Procedures and Instructions
 4. Records
 5. Quality Control in Sampling
 6. Quality Control in the Laboratory (including interlaboratory cross-check samples)
 7. Review and Analysis of Data (including criteria for recognizing deficiencies in data and provisions for investigation and correction of recognized deficiencies)
 8. Audits
- c. Additional guidance on laboratory quality assurance is provided in the INPO "Good Practice" documents CY-701 and CY-702, EPA-600/4-79-019, ASTM 3856, and ASTM D 4210. Guidance on statistical quality control in the laboratory is given in the following documents: (1) "Quality Control for Analytical Performance," in EPA-600/4-79-019; (2) "Quality Control in Chemical Analysis," Subsection B of Section 104, in Standard Methods for the Examination of Water and Wastewater; (3) ASTM Standard D 4210-82, "Practice for Intra-laboratory Quality Control Procedures and a Discussion on Reporting of Low-Level Data," and (4) ASTM STP 15-D, "Presentation of Data and Control Chart Analysis."
- d. Procedures for chemical analysis should be based on well established methods of analysis. Methods for chemical analysis of water are compiled in the Annual Book of ASTM Standards, the Standard Methods for the Examination of Water and Wastewater, and EPA-600/4-79-020. Selected ASTM methods are listed in Appendix I of this procedure. Both the PWR Secondary Water Chemistry

Guidelines and the BWR Water Chemistry Guidelines include discussions of methods of analysis for recommended chemical determinations.

03.06 Implementation of a Quality Assurance Program for Chemical Measurements. Examination of the implementation of the quality assurance program for chemical measurements may include:

- a. reviews of the results of audits and appraisals performed by or for the licensee (since the last inspection of this area) and the adequacy of the licensee's responses to identified needs for corrective actions
- b. reviews of records of maintenance and calibration of continuous (on-line) monitors
- c. reviews of the results of inter-laboratory cross-checks
- d. reviews of the use of blind, spike, and replicate samples
- e. reviews of the use of control charts
- f. reviews of the use of approved laboratory procedures for chemical analysis including instrument calibration, preventive maintenance, and operation

03.07 Laboratory Safety

- a. Radiological health and safety in the laboratory are covered by other inspection procedures including, in particular, Inspection Procedures 83524 and 83724 (external occupational exposure control), 83525 and 83725 (internal exposure control), and 83526 and 83726 (control of radioactive materials and contamination, surveys, and monitoring).
- b. OSHA has regulatory responsibility for non-radiological health and safety in the work areas of NRC-licensed facilities and NRC licenses, including inspections (see NRC Manual Chapter 1007 and its Appendix). Therefore, it is not intended that NRC inspectors devote additional inspection time to this area. However, in conducting the other inspection activities required by this procedure, inspectors will necessarily be examining facilities, procedures, and practices that affect non-radiological health and safety. When non-radiological health and safety hazards are observed, they should be noted.
- c. Guidance on laboratory safety and OSHA regulations is included as Chapter 14 of EPA-600/4-79-019. Guidance on this subject is also provided in the report, "Prudent Practices for Handling Hazardous Chemicals in Laboratories," by a committee of the National Research Council/National Academy of Sciences (NRC/NAS). An article by McKusick (1981) summarizes the main conclusions and recommendations of that report. An NRC/NAS committee has also published a book on "Prudent Practices for Disposal of Chemicals from Laboratories."

79501-04 REFERENCES

04.01 NRC Documents

Safety Analysis Report Chapter 5, "Reactor Coolant and Connected Systems" (especially Sections 5.4.2 and 5.4.8); Chapter 9, "Auxiliary Systems" (especially Sections 9.3.2 and 9.3.4); Chapter 10, "Steam and Power Conversion Systems" (especially Sections 10.3.5, 10.4.6, and 10.4.8).

Branch Technical Position MTEB 5-3, "Monitoring of Secondary Side Water Chemistry in PWR Systems," (Appendix to Standard Review Plan 5.4.2.1, NUREG-0800).

NUREG-0800, Standard Review Plan, Section 9.3.2, Process and Post-Accident Sampling Systems."

____, Standard Review Plan, Section 9.3.4, "Chemical and Volume Control System (PWR) (Including Boron Recovery System)."

____, Standard Review Plan, Section 10.4.6, "Condensate Cleanup."

____, Standard Review Plan, Section 10.4.8, "Steam Generator Blow Down System (PWR)."

Regulatory Guide 1.33, "Quality Assurance Program Requirements (Operation)."

____, 1.56, "Maintenance of Water Purity in Boiling Water Reactors."

____, 4.15, "Quality Assurance for Radiological Monitoring Programs (Normal Operations) - Effluent Streams and the Environment."

IE Manual Chapter 9900 (Guidance), Applicability of Appendix B to Chemicals and Reagents."

IE Information Notice, 82-32, "Contamination of Reactor Coolant System by Organic Cleaning Solvents," August 19, 1983.

____, 83-49, "Sampling and Prevention of Intrusion of Organic Chemicals into Reactor Coolant Systems," July 25, 1983.

04.02 Industry Standards

1983 Annual Book of ASTM Standards, Section 11, Water and Environmental Technology, Volumes 11.01 Water (I) and 11.02 Water (II).

Standard Methods for the Examination of Water and Wastewater, 15th Edition, American Public Health Association, 1980.

ASTM D 1066, "Practice for Sampling Steam."

ASTM D 1125, "Test Methods for Electrical Conductivity and Resistivity of Water."

ASTM D 3370, "Practices for Sampling Water."

ASTM D 3856-80, "Evaluating Laboratories Engaged in Sampling and Analysis of Water and Waste Water."

ASTM D 4210, "Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data."

INPO 82-007, INPO Guideline, "Chemistry Technician Qualification," September 1982.

INPO Good Practice CY-701, "Quality Control Program for Chemistry Instrumentation," INPO 83-016, May 1983.

INPO Good Practice CY-702, "Verification of Analytical Performance," INPO 83-017, May 1983.

INPO SOER, "Intrusion of Resin, Lubricating Oil, and Organic Chemicals into Reactor Coolant Water," December 13, 1982.

INPO 82-001-OEN-05, Good Practices, "Reduction of PWR Radiation Level Buildup by Maintenance of High Reactor Coolant pH," November 1982.

EPRI NP-2704-SR (Special Report), "PWR Secondary Water Chemistry Guidelines," Revision 1, June 1984.

BWR Owners Group Water Chemistry Guidelines Committee, "BWR Water Chemistry Guidelines," April 1, 1984.

04.03 General

EPRI NP-1603, "Water Quality in Boiling Water Reactors," Nov. 1980.

EPRI NP-2978, "State-of-the-Art Evaluation of Condensate Polisher Performance," April 1983.

EPRI NP-3020, "Evaluation and Improvement of PWR Secondary System Oxygen Control Measures," July 1983.

EPRI NP-3114-SY (Volume 1: Executive Summary), "BWR Radiation Assessment and Control Program: Assessment and Control of BWR Radiation Fields," May 1983.

EPRI NP-3207-SR, "Workshop Proceedings: Replacement/Repair of Steam Generators, Section 2, "Minimizing the Need for Steam Generator Replacements and Major Repairs," August 1983.

EPRI NP-3220, "Cobalt Contamination Resulting from Valve Maintenance," August 1983.

EPRI NP-3245, "Effects of Cold Shutdown Chemistry on PWR Radiation Control," September 1983.

EPRI NP-3463, "Coolant Chemistry Effects on Radioactivity at Two Pressurized Water Reactor Plants," March 1984.

EPRI NP-3513, "Post-Accident Liquid Sampling Systems."

ASTM STP 15D, ASTM Manual on "Presentation of Data and Control Chart Analysis," ASTM 1976.

Taylor, John J., "BWR Water Chemistry," EPRI Journal, pp. 52-54, January/February 1983.

Taylor, John J., "Controlling PWR Radiation Fields," EPRI Journal pp 56-58, May 1983.

Taylor, John J., "Influence of BWR Chemistry on Pipe Cracking," EPRI Journal, pp 58-59, June 1984.

Strauss, Sheldon D., "Polishing cuts condensate impurities below 0.1-ppb level," Power, pp 18-24, October 1984.

"LWR Coolant Impurity Control" EPRI Journal, pp 56-59, Sept. 1984

Wood, C. J., "Current Status and Future Direction of the EPRI Radiation Control Program," Radiation Protection Management 1 (No. 2), 65-75 (Jan. 1984).

EPA-600/4-79-019, "Handbook for Analytical Quality Control in Water and Waste Water Laboratories," U.S. Environmental Protection Agency, March 1979.

EPA-600/4-79-020, "Methods for Chemical Analysis of Water and Wastes," Revised March 1983.

McKusick, Blaine, C., Prudent Practices for Handling Hazardous Chemicals," Science, 211, 777-780 (20 February 1981).

Siegwarth, D. P., "Trends in Chemical Analysis Procedures at Nuclear Power Plants," Trans. American Nuclear Society 45, 638-639, Oct-Nov 1983.

National Research Council/National Academy of Sciences, Prudent Practices for Handling Hazardous Chemicals from Laboratories, 1983.

National Research Council/National Academy of Sciences, Prudent Practices for Disposal of Chemicals from Laboratories, 1983.

Cohen, Paul, Water Coolant Technology of Power Reactors, American Nuclear Society, Second Printing 1980.

ASTM STP 742, "Power Plant Instrumentation for Measurement of High Purity Water Quality," American Society for Testing Materials, 1981.

Inhorn, Stanley M., Quality Assurance Practices for Health Laboratories, American Public Health Assoc., 1978.

"Air Intrusions into BWR Primary Systems," Memorandum from J. E. Wigginton to R. R. Bellamy and other Regional Branch Chiefs, April 15, 1983.

END

APPENDIX I

SELECTED 1983 ASTM STANDARDS

VOLUMES 11.01 WATER (I) AND 11.02 WATER (II)

(Note: Asterisks denote standards referred to in industry water chemistry control guideline documents)

Definitions, Specifications, Reporting Results and Quality Control

- D 596-83, reporting results
- D 1129-82b, definitions
- D 1193-77, (1982), reagent water
- D 2777-77, precision and bias
- D 3856-80, evaluating laboratories
- D 4127-82, terms, ion-selective electrodes
- D 4210-82, intralaboratory QA and reporting low-level data
- *E 200-75 (1981), preparation, standardization, and storage of standard solutions

Sampling and Flow Measurement

- D 887-82, sampling water-formed deposits
- *D 1066-82, sampling steam
- *D 1192-70 (1977), equipment for sampling water and steam
- D 2687-84, sampling particulate ion-exchange materials
- *D 3370-82, sampling water

On-Line (Continual) Monitoring

- *D 1125, conductivity and resistivity
- *D 2791-77, sodium
- D 3864-79, continual on-line monitoring systems

General Properties of Water

- D 1067-82, acidity or alkalinity
- D 1125-82, electrical conductivity and resistivity
- D 1126-80, hardness in water
- *D 1293-78, pH
- D 1888-78, particulate and dissolved matter
- D 1889-81, turbidity
- D 2688-83, corrosively (weight loss methods)

Inorganic Constituents

- D 511-82, calcium and magnesium
- *D 512-81, chloride
- D 513-82, carbon dioxide, bicarbonate, and carbonate
- D 514-80, hydroxide ion
- D 515-82, phosphorus
- D 516-80, sulfate
- D 857-79, aluminum
- *D 859-80, silica
- *D 888-81, dissolved oxygen

- *D 1068-84, iron
- D 1179-80, fluoride
- D 1246-82a, iodide and bromide
- D 1339-78, sulfite
- *D 1385-78 (1982), hydrazine
- *D 1426-79, ammonia nitrogen
- *D 1428-82, sodium and potassium by flame photometry
- D 1588-60 (1974), hydrogen, dissolved and gaseous
- D 1687-80, chromium
- *D 1688-82, copper
- D 1691-77, zinc
- D 1886-84, nickel
- D 3082-79, boron
- D 3558-84, cobalt
- D 3590-84, nitrogen, Kjeldahl
- D 4191-82, sodium, atomic absorption
- D 4192-82, potassium, atomic absorption
- D 4327-84, Test Method for Anions in Water by Ion Chromatography

Carbon and Organic Constituents

- D 2579-78, total and organic carbon
- D 4129-82, total and organic carbon, coulometric

Ion-Exchange Resins

- D 2187-82, ion-exchange resins, physical and chemical properties

END